Chem 452 – Exam I
September 19, 2007

Cover Sheet
Closed Book, Closed Notes, and NO Calculator

There are 14 total pages. Each part of a question is worth 4 points unless otherwise noted.

Useful Equations:

\[ \Psi_n(x) = \left( \frac{2}{L} \right)^{1/2} \sin \left( \frac{n\pi x}{L} \right), \quad E_n = \frac{n^2 \hbar^2}{8mL^2} \]

\[ \Psi_{n_1,n_2}(x,y) = \left( \frac{2}{L_1} \right)^{1/2} \left( \frac{2}{L_2} \right)^{1/2} \sin \left( \frac{n_1\pi x}{L_1} \right) \sin \left( \frac{n_2\pi y}{L_2} \right) \]

\[ E_{n_1,n_2} = \frac{\hbar^2}{8m} \left( \frac{n_1^2}{L_1} + \frac{n_2^2}{L_2} \right) \]

\[ \lambda = \frac{\hbar}{p}, \quad p = mv \]
## Point Total

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<th>Problem</th>
<th>Possible Score</th>
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1. (20 points) Below is the potential energy of a particle in an infinite “box”. The wavefunction and energy expression are given on the cover sheet.
a. Write down the Hamiltonian for this system. Give the explicit functional forms for the operators.

b. Sketch on the diagram the first three energy levels \( n = 1, 2, 3 \).

c. Sketch on the diagram the wavefunction for the first excited state \( n = 2 \).

d. Sketch on the diagram the probability density for finding the particle as function of \( x \) for the second excited state \( n = 3 \).

e. For the first excited state, give the integral expression for the probability of finding the particle between \( x = L/2 \) and \( x = L \). Give the probability or evaluate the integral.
2. (8 points) The solution of the particle in a 1-dimensional “box” can be applied to mobile \( \pi \)-electrons in polymethine dyes similar to the \( \beta \)-carotene example in the text. Assume that each energy level in the box is capable of holding no more than two electrons and that the electronic transition responsible for the dye color corresponds to the promotion of an electron from the highest filled to the lowest empty level, the levels having initially been filled starting with the lowest. Assume that the molecule of interest has 14 \( \pi \)-electrons.

a. Write down the expression for \( \Delta E \) for the transition. Include the specific quantum numbers of the transition. There is no need to evaluate the expression.

b. How would \( \Delta E \) change if the box size and the number of electrons were both doubled?
3. (8 points) For a particle in a 2-dimensional square “box” \((L_1 = L_2 = L)\), there are two quantum numbers, \(n_1\) and \(n_2\) for the x and y directions, respectively. Relevant equations are on the cover.

a. Give the quantum numbers and degeneracy of the ground state.

b. Give the quantum numbers and degeneracy of the first excited state.
4. (8 points) Einstein discovered the photoelectric effect. The metal potassium has a work function of 2.25 eV.

   a. Make a plot of kinetic energy vs energy of the incident light. Use energy units of eV.

   b. Calculate the kinetic energy of the electrons ejected by light with energy 2.28 eV.
5. (12 points) Choose 3 of the 4 to answer. **Clearly mark which part you do not want graded.**

Answer the questions, giving a reason. Consider the operator \( \hat{O} = \frac{d}{dx} \).

a. Is the function \( \sin(ax) \) an eigenfunction of \( \hat{O} \)?

b. Is the function \( e^{kx} \) an eigenfunction of \( \hat{O} \)?

c. Is the function \( e^{\beta x^2} \) an eigenfunction of \( \hat{O} \)?
6. (8 points) For a particle in a one-dimensional “box” evaluate the following integrals. Give your logic for your answer.

a. \[ \int_{0}^{L} \sqrt[2]{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right) \sqrt[2]{\frac{2}{L}} \sin\left(\frac{3\pi x}{L}\right) dx \]

b. \[ \int_{0}^{L} \sqrt[2]{\frac{2}{L}} \sin\left(\frac{3\pi x}{L}\right) \sqrt[2]{\frac{2}{L}} \sin\left(\frac{3\pi x}{L}\right) dx \]
7. (4 points) The ground state of a system is non-degenerate and the first excited state is 3-fold degenerate. The difference in energy between the two states is $\Delta E$. Write down the ratio of populations of particles in the first excited state to the ground state.

8. (4 points) One of the lecture problems discussed estimation of the de Broglie wavelength of a heavy tennis ball of mass 66 g traveling at 80 km/h. The de Broglie wavelength is $4.5 \times 10^{-34}$ m. What is the de Broglie wavelength of the argon atom of mass $66 \times 10^{-27}$ kg traveling with the same speed?
9. (8 points) For the particle in a one-dimensional “box” with infinite walls at $x = 0$ and $x = L$ for $n = 3$.

   a. Write down the expression for the average position of the particle.

   b. Use logic to evaluate this expression. Explain your logic.
MULTIPLE CHOICE (circle your answer)

10. An important experimental confirmation of the de Broglie relation was provided by

   a. Measurement of the energy of black-body radiation as a function of wavelength.
   b. Measurements of the low temperature heat capacities of solids.
   c. Measurements of the energies of photoelectrons emitted by metals versus wavelength of incident light.
   d. Measurements of the intensity patterns of electrons scattered from a solid surface.
   e. None of the above.

11. Which statement is true? Planck’s assumption that the oscillators in the walls of a black-body radiator have quantized energies

   a. required the assumption that different metals have different work functions.
   b. predicted a frequency of maximum power output that is independent of temperature.
   c. overcame the ultraviolet catastrophe.
   d. explained the line spectra in black-body emissions.
   e. None of the above is a true statement.
12. Which one of the following is a **false** statement for the particle in a one-dimensional “box” with infinite walls at \( x = 0 \) and \( x = L \)?

   a. When \( n = 1 \), the probability distribution for the particle is uniform (i.e., constant from \( x = 0 \) to \( x = L \)).

   b. As \( n \) increases, the energy levels get closer together.

   c. When \( n = 2 \), the probability for finding the particle on one side of the “box” is positive, and the probability for finding it on the other side is negative.

   d. As \( L \) decreases, the energy levels get farther apart.

   e. All of the above statements are false

13. It is found that a particle in a one-dimensional “box” of length \( L \) can be excited from the \( n = 1 \) to the \( n = 2 \) state by light of frequency \( \nu \). If the “box” length is doubled, the frequency needed to produce the \( n = 1 \) to the \( n = 2 \) transition becomes

   a. \( \nu / 4 \)

   b. \( \nu / 2 \)

   c. \( 2\nu \)

   d. \( 4\nu \)

   e. None of the above is correct.
14. Which statement is true?

a. Tunnelling is the leakage by penetration through a classically forbidden region.

b. The tunneling probability (transmission probability) is larger for smaller masses.

c. The tunneling probability (transmission probability) is larger for narrower potential barriers.

d. The tunneling probability (transmission probability) is larger for energies almost at the top of the potential barrier rather than at the bottom of the barrier.

e. All the above statements are true.